

Monomer Basis Representation Method For Calculating The Spectra Of Molecular Clusters I. The Method And Qualitative Models.

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(Dated: March 1, 2013)

Abstract

Firstly, a sequential symmetry adaptation procedure is derived for semidirect product groups. Then, this sequential symmetry adaptation procedure is used in the development of new method named Monomer Basis Representation (MBR) for calculating the vibration-rotation-tunneling (VRT) spectra of molecular clusters. The method is based on generation of optimized bases for each monomer in the cluster as a linear combination of some primitive basis functions and then using the sequential symmetry adaptation procedure for generating a small symmetry adapted basis for the solution of the full problem. It is seen that given an optimized basis for each monomer the application of the sequential symmetry adaptation procedure leads to a generalized eigenvalue problem instead of a standard eigenvalue problem if the procedure is used as it is. In this paper, MBR method will be developed as a solution of that problem such that it leads to generation of an orthogonal optimized basis for the cluster being studied regardless of the nature of the primitive bases that are used in the generation of optimized bases of the monomers.

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I. INTRODUCTION

Obtaining the bulk properties of condensed phases from microscopic considerations is a long standing dream. For that purpose, it is essential to develop an accurate potential surface.

The total potential energy function $V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N)$ of a system of N identical particles can be expanded as sum of n -body potentials:

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i_1 < i_2}^N V_2(\vec{r}_{i_1}, \vec{r}_{i_2}) + \sum_{i_1 < i_2 < i_3}^N V_3(\vec{r}_{i_1}, \vec{r}_{i_2}, \vec{r}_{i_3}) \\ + \dots + \sum_{i_1 < i_2 < i_3, \dots, i_N}^N V_n(\vec{r}_{i_1}, \vec{r}_{i_2}, \vec{r}_{i_3}, \dots, \vec{r}_{i_N}). \quad (1)$$

It has been assumed in the past that this series converges rapidly and in most systems the pairwise additive approximation, i.e.

$$V(\vec{r}_1, \vec{r}_2, \dots, \vec{r}_N) = \sum_{i_1 < i_2}^N V_2(\vec{r}_{i_1}, \vec{r}_{i_2}), \quad (2)$$

has been shown to be qualitatively valid. However, this is not the case for many systems [1–4]. For example, the higher order terms in equation (1) may add up to 25% of the interaction energy of bulk water [5], most of which results from three-body effects. It has been found that [6] the pair interaction energy represents 83 – 86% of the total interaction energy of $(H_2O)_3 \approx 75\%$ of $(H_2O)_4$ and only $\approx 68\%$ of $(H_2O)_5$. Therefore, it is evident that many-body terms are far from negligible.

Before the studies of van der Waals molecules, most experiments sensitive to many-body effects were performed on macroscopic systems with the result that only the *total* many body effects were obtained. Then, condensed phase properties have been used to determine “effective” pair potentials [7] which include all of the terms in the many-body expansion in an average manner, at least over some range of temperature.

On the other hand, studies of small clusters proved to be ideal for studying many-body terms, because each term in the many-body expansion can be studied uniquely. For example, dimers are ideal for studying two-body potentials, since there are no many-body terms in their potential surfaces. Similarly, once the potential surface of the dimer of a substance is known accurately, the trimer of that substance becomes the model system for studying

three-body terms in its potential surface, because three-body terms are the only many-body terms in the potential surface of a trimer. Thus, in principle it is possible to develop accurate potential surfaces by starting from dimers and deriving the many-body terms by studying bigger and bigger clusters. However, it is very hard to accomplish in practice. In order to develop a potential surface or in order to test the accuracy of an available potential surface, it is necessary to make quantum mechanical calculations. In quantum mechanical spectra calculations, the eigenstates of the Hamiltonian operator are usually obtained by diagonalizing the matrix representing the Hamiltonian operator in a finite basis and it is well known that the size of the basis required for the calculations grows exponentially with the number of degrees of freedom. As a result of that, the quantum mechanical calculations becomes harder as the size of the problem gets bigger.

Considering inter-molecular vibrations of molecular clusters (consisting of nonlinear monomers), dimers are six dimensional systems and trimers are twelve dimensional systems. If it is possible to obtain accurate results with N basis functions per degree of freedom, then a dimer calculation requires N^6 basis functions and a trimer calculation requires N^{12} basis functions. Even if it would be possible to obtain good results with a small number of basis functions per degree of freedom such as $N = 10$, the size of a basis required for a trimer calculation would be a million times bigger than the size of a basis required for a dimer calculation. It is this exponential scaling of the number of the basis functions which makes the calculations harder and harder as the size of the problem gets bigger, and obviously it is necessary to develop methods for reducing the size of the bases.

One way of reducing the sizes of bases is to make symmetry adaptation of basis functions and solve for each symmetry separately. However, the well-known method of symmetry adaptation is not very helpful. Although, the sizes of bases grow exponentially, orders of molecular symmetry groups [8] grow linearly. For example, order of the molecular symmetry group of water dimer is 16 [9] and the order of the molecular symmetry group of water trimer is 48 [10].

A much more efficient way of reducing the computational cost is to use bases that are optimized for the particular problem at hand instead of primitive bases. The inefficiency of primitive bases results from the fact that they do not know anything about the potential surface of the system. The optimized bases that know about the underlying potential surface can be generated as linear combinations of some primitive basis functions by taking a model

potential surface that resembles to the actual potential surface as much as possible and solving for its eigenstates. This obviously makes it necessary to divide the problem into smaller parts since trying to find an optimized basis for the full problem is as difficult as solving it. In the case of molecular clusters an obvious way of dividing the problem into smaller parts is to consider each monomer separately. In the rest of the paper, the main discussion will be about how optimized bases for each monomer can be generated and how they can be combined for the solution of the full problem.

In section II, a sequential symmetry adaptation procedure will be derived. By finding the relations between the projection operators of the irreducible representations of the molecular symmetry group of the cluster and the projection operators of the irreducible representations of its subgroups, symmetries of monomer basis functions will be related to the symmetries of eigenstates of the cluster. This symmetry adaptation procedure will be used in section III in which generation of optimized monomer bases is discussed. It will be seen that generation of optimized bases creates its own problems related with symmetry adaptation. In order to guarantee generation of an efficient orthonormal basis, it will be necessary to modify the sequential symmetry adaptation procedure developed in section II. In order to illustrate how the method can be used for generating small symmetry adapted bases, two qualitative models will be given in section V, one for water dimer and one for water trimer. The method will be applied to water dimer in a forthcoming paper in order to illustrate its application and to show its validity.

II. SEQUENTIAL SYMMETRY ADAPTATION

An analysis of the structure of the molecular symmetry groups shows that the molecular symmetry group of a molecular cluster consisting of n non-reacting monomers can be written in terms of its subgroups as [11]

$$G(MS) = ((G_{k_1} \otimes G_{k_2} \otimes \dots \otimes G_{k_n}) \mathbb{S} G_l) \otimes \varepsilon. \quad (3)$$

In the equation above, the groups G_{k_i} with $i = 1, \dots, n$ are the pure permutation subgroups of the monomers that have orders k_i ; the group G_l which is of the order of l is the subgroup containing the operations permuting the identical monomers; and the group ε is the inversion subgroup that contains the identity element E and the inversion element E^* .

In equation (3), \otimes denotes a direct product multiplication and $\textcircled{\text{S}}$ denotes a semi-direct product multiplication. The difference between a direct product and a semi-direct product multiplication is that in a direct product multiplication both of the subgroups are invariant subgroups of the product group while in a semi-direct product multiplication only one of them is an invariant subgroup of the product group. Since the operations permuting the identical monomers bring in non-commutation, presence of a semi-direct product multiplication is inevitable. In this paper, it will be assumed that the group G_l is cyclic and has the order $l = n_m$. In the case of dimers the order of the group which contains the permutations of identical monomers has to be 2 anyway (since $n_m! = n_m$ for $n_m = 2$), so that there is no assumption. However, in the case of bigger clusters, physical meaning of this assumption is that the cluster is assumed to have a rigid cyclic skeleton. The reason for this assumption will be clear in section IIIB. It should be noted that equation (3) assumes that the inversion operation is a feasible symmetry operation of the molecular symmetry group which is not true in general. However, this corresponds to a more general case. The method developed in this paper is applicable to any cluster whose molecular symmetry group does not include inversion operation, too.

Symmetry adaptation of basis functions to an irreducible representation Γ of a group G can be done by application of the projection operator of that irreducible representation which is given by [12, 13]

$$\hat{P}_G^\Gamma = \frac{d_\Gamma}{|G|} \sum_{g \in G} \chi^\Gamma[g]^* \hat{O}_g, \quad (4)$$

where g are the elements of the group G , d_Γ is the dimension of the irreducible representation Γ , $|G|$ is the order of the group G , \hat{O}_g is the operator representing g , and $\chi^\Gamma[g]$ is the character of g in the irreducible representation Γ . As shown in the appendix, for a group G that can be written as a semi-direct product of two of its subgroups H and K , and satisfying the condition given in equation (44), the projection operator of an irreducible representation can be decomposed into product of two terms such that

$$\hat{P}_G^\Gamma = \left(\frac{1}{|H|} \sum_{h \in H} \chi^\Gamma[h]^* \hat{O}_h \right) \left(\frac{1}{|K|} \sum_{k \in K} \chi^\Gamma[k]^* \hat{O}_k \right), \quad (5)$$

where the definitions of the terms are similar to those of equation (4). Please note that the condition given in equation (44) is always satisfied for any direct product group. Therefore, equation (5) applies to all of the group multiplications in equation (3). Consequently, it

follows that the symmetry adaptation of basis functions can be done in $n + 2$ steps sequentially. Furthermore, the characters in equation (5) can be decomposed to their irreducible components in groups H and K . Thus, if the character in the first parentheses in equation (5), can be expressed as $a_1\Gamma_1 \oplus a_2\Gamma_2 \oplus \dots$ where a_i are nonnegative integers and Γ_i are the irreducible representations of the group H , then from the definition of projection operators it follows that this parentheses can be expressed in terms of the projection operators of the irreducible representations of the group H as

$$\frac{1}{|H|} \sum_{h \in H} \chi^\Gamma[h]^* \hat{O}_h = \frac{a_1}{d_1} \hat{P}_H^{\Gamma_1} + \frac{a_2}{d_2} \hat{P}_H^{\Gamma_2} + \dots, \quad (6)$$

where $\hat{P}_H^{\Gamma_i}$ is the projection operator and d_i are the dimension of the irreducible representation Γ_i . A similar expression can also be written for the second parentheses in equation (5) in terms of the projection operators of the irreducible representations of the group K . Obviously only the terms for which a_i is nonzero will contribute to the sum. Consequently, equation (6), or equally finding the coefficients a_i is useful for determining which symmetries of the monomer basis functions can be symmetry adapted to an irreducible representation of the product group.

III. MONOMER BASIS REPRESENTATION METHOD

If the symmetry adaptation procedure given in previous section is used with primitive bases, it can not provide any optimization more than what one can achieve with the direct symmetry adaptation by using equation (4). On the other hand, sequential symmetry adaptation procedure combined with the physically meaningful partitioning of the molecular symmetry groups given in equation (3) makes it possible to devise algorithms for obtaining symmetry adapted optimized bases.

On the other hand, generation of optimized bases creates its own problems related with symmetry adaptation. Primitive basis functions (plane waves, spherical harmonics, Wigner rotation functions ...) are the solutions of Hamiltonians corresponding to motions of free particles or free bodies. Since the kinetic energy is always absolutely symmetric, a free particle Hamiltonian has absolute symmetry, too. Consequently, the basis functions that are obtained as solutions of that Hamiltonian also have absolute symmetry. As a result of that application of a symmetry operation to a primitive basis function always results in

another function in the same basis other than a possible phase factor. Thus the symmetry adapted basis functions can be obtained as linear combinations of primitive basis functions.

The case of optimized basis functions is different. An optimized basis function should know about the particular problem at hand so that the Hamiltonian, that the optimized basis functions are solutions of, should include a potential energy function. Since the potential surfaces do not have absolute symmetry, a Hamiltonian including a potential energy function can not be absolutely symmetric, either. This will restrict the symmetries of optimized basis functions that are obtained as solutions of the Hamiltonian. This means that application of a symmetry operation to an optimized basis function will not necessarily result in another basis function in the same optimized basis. As a result of that solving a problem might be impossible when optimized basis functions are used unless a special care is taken to ensure that the physically meaningful solutions of the Hamiltonian can be obtained as linear combinations of the optimized basis functions.

A discussion of how such optimized monomer bases can be found and how they can be combined for the solution of the full problem will be made in the following subsections. The procedure for obtaining the results can be divided into four steps. These steps are: generation of a basis for one of the monomers, generation of bases for other monomers, combining monomer bases to generate a basis for the full problem, and the solution of the full problem.

Before starting to develop the method, it should be noted that a basis function related with a monomer is a function which describes the orientation of the monomer in the cluster and a function related with inter-monomer coordinates is a function which describes the orientation of the monomers with respect to each other. The monomers are assumed to be rigid bodies so that intra-monomer degrees of freedom are not considered. In the discussion, language of Permutation Inversion (PI) group theory [8, 12, 14] will be used since it provides the most natural way of handling the symmetries in molecular systems.

A. Generation of A Monomer Basis

In order to have a basis which is fully symmetry adapted, or can be fully symmetry adapted, to the molecular symmetry group of the cluster, there should be a basis for each monomer, which is symmetry adapted to the irreducible representations of the pure per-

mutation group of the monomer G_k . This can be done by just taking a primitive basis for each monomer, and then symmetry adapting it to the irreducible representations of the permutation group, G_k . However, in order to have an efficient basis for the full problem, the size of the monomer basis should be small; and just taking a small number of primitive basis functions for each monomer will not be a good choice obviously. Therefore, instead of using a primitive basis for each monomer, which does not know anything about the problem at hand, it is better to have a basis which is optimized for the particular problem being studied.

An optimized basis for a monomer can be generated by taking a model Hamiltonian for that monomer and then solving for the eigenstates of the model Hamiltonian with a basis which has the required symmetry properties. Then, a small number of the eigenstates of the model Hamiltonian can be taken as an optimized basis for that monomer. The model Hamiltonian should include the kinetic energy operator related with that monomer in the Hamiltonian of the cluster and a model potential surface for that monomer. The model potential surface can be chosen as desired. However, the efficiency of the resulting basis will depend on this choice.

The primitive basis functions which are used to generate the optimized basis should be symmetry adapted by using the operations contained in the pure permutation group related with that monomer. According to equation 5, this is certainly sufficient for making sequential symmetry adaptation properly. However, in order to guarantee invariance of the cluster basis while combining the monomer bases, it is better to follow a more complex path for making sequential symmetry adaptation of basis functions because of the reasons explained below.

If the sequential symmetry adaptation procedure is used as it is, then the basis functions are going to be symmetry adapted to the irreducible representations of the inversion subgroup while forming the symmetry adapted cluster basis functions. At this step, it will be necessary to apply inversion operation, E^* to the monomer basis functions. When the inversion operation is applied to a basis function of a monomer, the result will be another basis function for the same monomer. However, the resulting function will not be in the same basis unless the basis has the inversion symmetry of the *cluster*. Since the optimized basis functions of the monomers are going to be generated with a calculation, the basis functions cannot have such a symmetry unless the model potential surface of the cluster has the in-

version symmetry of the cluster. A model potential surface for a monomer cannot have such a property unless it is imposed to it. Consequently, if the sequential symmetry adaptation procedure is used as it is, it will be necessary to deal with a generalized eigenvalue problem instead of a standard eigenvalue problem.

This problem can be overcome by using the properties of direct product groups. The inversion subgroup can always be multiplied with another subgroup of the molecular symmetry group with direct product multiplication. If the basis functions that are used to generate optimized monomer bases are symmetry adapted to irreducible representations of the direct product group obtained from the pure permutation group of the monomer and the inversion subgroup of the cluster. Then, they will be symmetry adapted to the irreducible representations of both the pure permutation group of the monomer and the inversion subgroup of the cluster. In this case, the application of the inversion operation to optimized basis functions will not create new functions. In fact, they will be the eigenstates of the inversion operation with the eigenvalues ± 1 . If the same thing is true, for all of the monomer bases, then the product basis of the monomer bases will also be eigenstates of the inversion operation with the eigenvalues ± 1 . Consequently, the product basis of the monomer bases will be invariant under the effect of the inversion operation so that the symmetry adaptation of basis functions will not lead to a generalized eigenvalue problem but to a standard eigenvalue problem.

To sum up, in order to generate a small basis for a monomer, the permutation group of that monomer, G_k , and the inversion subgroup, ε , of the molecular symmetry group of the *cluster* are taken and the direct product group of these two subgroups are formed. Then, the eigenstates of the model Hamiltonian is solved for each symmetry separately after the basis functions are symmetry adapted. A subset of these eigenstates becomes the contracted basis for that monomer.

B. Generation of Bases for Other Monomers

The procedure given in section III A can be used for generating a contracted basis for each of the monomers. However, this will not be the optimal choice. Because, the molecular symmetry group of the cluster includes the subgroup which includes the operations permuting the identical monomers as a subgroup. Therefore, after the monomer bases are

combined together they are going to be symmetry adapted by using the symmetry operations contained in this group. The permutation operations in this group will mix the monomer bases, such that when these permutation operations are applied to the basis functions of a monomer, then the resulting function will be a basis function for another monomer. If this resulting basis function is not already available in the contracted basis of that monomer, then it will not be orthogonal to the basis functions of that monomer necessarily. Therefore, unless there is a relation between the bases of different monomers, symmetry adaptation to the group which includes the operations permuting the identical monomers will always be a problem. As a result of that, a better way of constructing bases for all of the monomers is to find a basis for one of them, and then to generate bases for other monomers from the basis of this monomer.

The obvious choice for generating the bases for other monomers could be just to relabel the basis functions of a single monomer for different monomers. However, this will not help to get rid of the symmetry adaptation problem posed before. If the monomer basis functions are generated with relabeling, the basis functions obtained in this way will be symmetry adapted in their own permutation groups since these groups are isomorphic to each other. However, if the permutation operations which permute the identical monomers has some effect on the coordinates other than relabeling them, the action of these permutation operations to basis functions will still result in new basis functions. Although relabeling the basis functions of the first monomer to generate bases for the other monomers can be a solution for some specific cases, where the action of the permutation operations is just to relabel the coordinates (in fact this would be the case if Cartesian coordinates were used), it is not applicable in general, and is far from being a general solution.

The general solution to that symmetry adaptation problem can be found as follows. Firstly, let's consider the case of a dimer. If the monomers are labeled as a and b , then the group which contains the permutations of identical monomers will be $G_2 = \{E, P_{ab}\}$, where the operation P_{ab} is the permutation operation which permutes the monomers a and b . If $\phi_k^{(a)}$ is the k^{th} basis functions in the optimized basis of the monomer a and $\phi_l^{(b)}$ is the l^{th} function in the optimized basis of the monomer b (which is to be determined), then $\phi_k^{(a)}\phi_l^{(b)}$ will be one of the product basis functions. In order to make symmetry adaptation of the basis functions, it will be necessary to apply the permutation operation P_{ab} to the basis functions. The application of the operation P_{ab} will relabel the basis functions, but it will

also introduce some changes to them so that the new basis function obtained by application of this operation will be

$$P_{ab}\phi_k^{(a)}\phi_l^{(b)} = \phi_k^{(b)'}\phi_l^{(a)'}, \quad (7)$$

where $\phi_k^{(b)'} = P_{ab}\phi_k^{(a)}$ and $\phi_l^{(a)'} = P_{ab}\phi_l^{(b)}$. The resulting basis functions are labeled with 's to imply that they are not necessarily in the bases of monomers a and b . At this point it can be realized that the problem can be get rid of by defining

$$\phi_k^{(b)} = P_{ab}\phi_k^{(a)}. \quad (8)$$

Thus, equation (7) becomes,

$$P_{ab}\phi_k^{(a)}\phi_l^{(b)} = P_{ab}(\phi_k^{(a)}(P_{ab}\phi_l^{(a)})) \quad (9)$$

$$= (P_{ab}\phi_k^{(a)})(P_{ab}P_{ab}\phi_l^{(a)}) \quad (10)$$

$$= \phi_k^{(b)}\phi_l^{(a)}. \quad (11)$$

In the equations above $P_{ab}P_{ab} = E$ is used that is permuting the two monomers between them twice is equivalent to the application of the identity operation, so that it leaves the system invariant (In other words, P_{ab} is its own inverse: $P_{ab}^\dagger = P_{ab}$).

Thus, if the basis functions for the monomer b are generated by using equation (8), then the application of the permutation operation P_{ab} does not generate new basis functions but just carries a basis function in the basis of a monomer to another basis function in the basis of the other monomer.

Although, the discussion above is made for just two monomers, the idea can be extended to any bigger cluster. In the case of a trimer, for example, if the monomers are labeled as a , b and c , the cyclic group containing the permutations of identical monomers will be the group $G_3 = \{E, P_{abc}, P_{acb}\}$. In this case the basis of the monomer b can be generated by

$$\phi_k^{(b)} = P_{abc}\phi_k^{(a)}. \quad (12)$$

The basis of the monomer c can be generated from the basis of monomer b by

$$\phi_k^{(c)} = P_{abc}\phi_k^{(b)}. \quad (13)$$

Thus, by repeated application of the generator of the group G_3 , it is possible to generate bases for all of the three monomers from the basis of a single monomer. This method can be extended to any bigger cluster.

If the group G_l is the cyclic group with the order n_m , then a basis for all of the monomers can be generated from the basis of a single monomer by repeated application of the generator of the group G_l . The reason for the assumption that the group G_l is cyclic should be clear at this point. For example, in the case of a trimer if the group containing the permutations of the identical monomers would be the group $G_6 = \{E, P_{abc}, P_{acb}, P_{ab}, P_{ac}, P_{bc}\}$, there would be more than one way of generating bases for other monomers. For example, both of the operations P_{abc} and P_{ab} can be used to generate a basis for the monomer b from the basis of the monomer a . If the operation P_{abc} (P_{ab}) is used; then, the application of the operation P_{ab} (P_{abc}) may still create new basis functions. In such a situation, it is impossible to guarantee the invariance of the basis.

Before closing this section, it should also be noted that a basis, which is generated by using the generator of the group which includes the operations that permute identical monomers, will have the same orthogonality relations with the original basis. For example, if one has an orthonormal basis for the monomer a , then the basis of the monomer b generated by using equation (8) will have

$$\begin{aligned}
\langle \phi_k^{(b)} | \phi_l^{(b)} \rangle &= \langle P_{ab} \phi_k^{(a)} | P_{ab} \phi_l^{(a)} \rangle \\
&= \langle \phi_k^{(a)} | P_{ab}^\dagger P_{ab} \phi_l^{(a)} \rangle \\
&= \langle \phi_k^{(a)} | \phi_l^{(a)} \rangle \\
&= \delta_{kl}
\end{aligned} \tag{14}$$

Besides, the basis functions of the monomer b will be eigenstates of the model Hamiltonian of the monomer b which is generated in the way that the eigenstates of the monomer b is generated. Thus, if \hat{H}_a^0 is the model Hamiltonian of the monomer a , and $\phi_k^{(a)}$ is the k^{th} eigenstate of this model Hamiltonian with the eigenvalue $\epsilon_k^{(a)}$ such that

$$\hat{H}_a^0 \phi_k^{(a)} = \epsilon_k^{(a)} \phi_k^{(a)}; \tag{15}$$

then, by applying the permutation operation to both sides of the equation above,

$$P_{ab} \hat{H}_a^0 \phi_k^{(a)} = P_{ab} \epsilon_k^{(a)} \phi_k^{(a)}, \tag{16}$$

and inserting the identity operation $P_{ab}^\dagger P_{ab} = E$ between Hamiltonian and the basis function one gets

$$P_{ab} \hat{H}_a^0 P_{ab}^\dagger P_{ab} \phi_k^{(a)} = \epsilon_k^{(a)} P_{ab} \phi_k^{(a)}. \tag{17}$$

Thus,

$$\hat{H}_b^0 \phi_k^{(b)} = \epsilon_k^{(a)} \phi_k^{(b)}, \quad (18)$$

where equation (8) is used, and \hat{H}_b^0 is defined as

$$\hat{H}_b^0 = P_{ab} \hat{H}_a^0 P_{ab}^\dagger. \quad (19)$$

Therefore, from equation (18), it follows that $\phi_k^{(b)}$ is an eigenstate of the model Hamiltonian \hat{H}_b^0 with the eigenvalue $\epsilon_k^{(b)} = \epsilon_k^{(a)}$, such that

$$\hat{H}_b^0 \phi_k^{(b)} = \epsilon_k^{(b)} \phi_k^{(b)}. \quad (20)$$

C. Combining Monomer Bases

After a basis for one of the monomers is generated by solving for the eigenstates of a model Hamiltonian, and the bases for the other monomers are generated from the basis of this monomer by using the generator of the group containing the permutations of identical monomers; a basis for calculating the spectra of the cluster can be generated by forming the tensor product of the monomer bases and combining them with a primitive basis for the inter-monomer coordinates. Thus, if $\phi_{n_k}^{(k)}$ is the n^{th} basis function for the monomer k and χ_l is the l^{th} basis function related with inter-monomer coordinates, the eigenstates of the full problem can be expanded in this product basis as

$$\Psi_i = \sum_{n_1, n_2, \dots, n_{n_m}, l} C_i^{n_1, n_2, \dots, n_{n_m}, l} \chi_l \prod_{k=1}^{n_m} \phi_{n_k}^{(k)}, \quad (21)$$

where $C_i^{n_1, n_2, \dots, n_{n_m}, l}$ is the expansion coefficient.

As discussed in the previous sections, the product basis of the monomer bases will be invariant under the effect of any permutation inversion operation. Since a primitive basis is used for the inter-monomer coordinates, it can be chosen to be invariant under the effect of any permutation inversion operation. Consequently, the eigenstates of the cluster can be obtained as linear combinations of the basis functions of this basis even if the basis is not symmetry adapted for calculations. However, symmetry adaptation is always useful for reducing the size of the basis.

The obvious way to make the symmetry adaptation of the basis functions to an irreducible representation of the molecular symmetry group of a cluster is to apply the projection operator of that irreducible representation to the basis functions.

Since the group $G_k \otimes \varepsilon$ which is used in monomer calculations contains the group G_k as an invariant subgroup, the monomer basis functions will already be symmetry adapted in their own pure permutation groups $G_k^{(s)}$. Therefore, symmetry adaptation of the basis functions can be done in two steps after finding the correlations between the irreducible representations of the molecular symmetry group and the irreducible representations of the pure permutation groups. For example, considering the bases of the monomer a if the irreducible representation Γ_α of the molecular symmetry group correlates to the irreducible representation Γ_i of the group $G_k^{(a)}$, then only the bases which are symmetry adapted to the irreducible representation Γ_i should be used for the calculations. The bases which are symmetry adapted to the other irreducible representations will be annihilated by the application of the projection operator of the group Γ_α , since this projection operator contains the projection operator $P_{G_k^{(a)}}^{\Gamma_i}$ of the group $G_k^{(a)}$. On the other hand, the application of the projection operator $P_{G_k^{(a)}}^{\Gamma_i}$ will leave the basis functions of the monomer a which are symmetry adapted to the Γ_i irreducible representation of the group $G_k^{(a)}$ invariant. Thus, if the correlations between the irreducible representations of the molecular symmetry group of the cluster and the pure permutation groups of the monomers are found and the appropriate bases are chosen, then the symmetry adaptation of the basis functions can be done in two steps by symmetry adapting the basis functions further to the groups G_l which is the group containing the permutations of the identical monomers and the inversion group ε .

Since monomer basis functions are symmetry adapted to the group $G_k \otimes \varepsilon$, there will be two bases which are symmetry adapted to two different irreducible representations of the group $G_k \otimes \varepsilon$ and at the same time which are symmetry adapted to the irreducible representation Γ_i of the group G_k . One of these bases will be symmetry adapted to the irreducible representation $\Gamma_i \otimes G = \Gamma_{ig}$, which will have even parity, and one of them will be symmetry adapted to the irreducible representation $\Gamma_i \otimes U = \Gamma_{iu}$ (see table II for the irreducible representations G and U of the group ε). Thus, if it is necessary to have a basis for the monomer a which is symmetry adapted to the irreducible representation Γ_i , then the basis which should be used for the monomer a will be

$$\Gamma_{ig} \oplus \Gamma_{iu},$$

where the labels of the irreducible representations are used to mean any basis function belonging to that symmetry. The bases of all of the monomers can be found similarly. Thus,

when the correlations are found and the product basis is formed there will be 2^{n_m} different product bases which differ from each other by the symmetries of monomer functions. Since inter-monomer coordinates are usually invariant under the effect of the inversion operation, half of these terms will have even parity and half of them will have odd parity. Thus, when the symmetry adaptation of the basis functions to the inversion group is done half of these terms will be annihilated and half of them will leave invariant. After finding the correlations, a fully symmetry adapted basis can be generated by symmetry adapting them by using the symmetry operations of the pure permutation group G_l . Thus, the symmetry adapted basis functions can be obtained as

$$\Psi^{(\Gamma_\alpha)} = \frac{1}{|G_l|} \sum_{g \in G_l} \chi^{\Gamma_\alpha}[g]^* \hat{O}_g \chi_l \prod_{k=1}^{n_m} \phi_{n_k}^{(k)}, \quad (22)$$

where Γ_α is an irreducible representation of the molecular symmetry group, and $\chi^{\Gamma_\alpha}[g]$ is the character of the operation g represented with the operation \hat{O}_g in the irreducible representation Γ_α .

D. Solution of The Full Problem

In order to find the eigenvalues of the Hamiltonian, the matrix elements of the matrix representing the Hamiltonian should be calculated. They can be evaluated easily if the Hamiltonian is partitioned as

$$\hat{H} = \sum_{k=1}^{n_m} \hat{H}_k^0 + \hat{\Delta T} + \hat{\Delta V}, \quad (23)$$

where \hat{H}_k^0 's are the model Hamiltonians for the monomers, $\hat{\Delta T}$ is the kinetic energy terms which are not included in the model Hamiltonians and $\hat{\Delta V} = \hat{V} - \sum_{k=1}^{n_m} \hat{V}_k^0$ is the difference between the potential surface of the full problem and the sum of the model potential surfaces used in the model Hamiltonians to determine the bases for the monomers.

The basis functions of the full problem become eigenstates of the zeroth order Hamiltonian for the full problem, such that by defining

$$\hat{H}^0 = \sum_{k=1}^{n_m} \hat{H}_k^0, \quad (24)$$

and expanding the wave function in the product basis

$$\psi_{n_1, n_2, \dots, n_{n_m}, l} = \chi_l \prod_{k=1}^{n_m} \phi_{n_k}^{(k)}, \quad (25)$$

the following eigenvalue relation is obtained

$$\hat{H}^0 \psi_{n_1, n_2, \dots, n_{n_m}, l} = \left(\sum_{k=1}^{n_m} \epsilon_{n_k}^{(k)} \right) \psi_{n_1, n_2, \dots, n_{n_m}, l}. \quad (26)$$

Therefore, the matrix elements of the Hamiltonian in the basis of the full problem will be given by

$$\begin{aligned} \langle \psi_{n'_1, n'_2, \dots, n'_{n_m}, l'} | \hat{H} | \psi_{n_1, n_2, \dots, n_{n_m}, l} \rangle &= \sum_{k=1}^{n_m} \epsilon_{n_k}^{(k)} \delta_{ll'} \prod_{r=1}^{n_m} \delta_{n_r, n'_r} \\ &+ \langle \psi_{n'_1, n'_2, \dots, n'_{n_m}, l'} | \hat{\Delta T} + \hat{\Delta V} | \psi_{n_1, n_2, \dots, n_{n_m}, l} \rangle. \end{aligned} \quad (27)$$

Thus, in order to calculate the matrix elements of the Hamiltonian, it is necessary to evaluate matrix elements of the $\hat{\Delta T}$ and $\hat{\Delta V}$ terms, in the basis of the full problem. These terms can be evaluated in the primitive bases of monomers and in the primitive basis of inter-monomer coordinates, then they can be transformed to the contracted basis of the cluster. If the terms $\hat{\Delta T}$ and $\hat{\Delta V}$ are small; then these terms can be considered as a small perturbation and the basis functions will resemble to the eigenstates of the actually problem. In such a case, convergence of the results can be obtained by using a small number of contracted basis functions. However, this may not be the case for many problems.

IV. FURTHER DETAILS ABOUT THE MBR METHOD

A. The Case of Non-identical Monomers

While discussing the method in section III, it was assumed that the cluster consist of identical monomers. However, this assumption can be relaxed easily.

If there are non-identical monomers in the cluster, then a monomer basis can be generated for each type of monomer separately in the way it is discussed in section III A. In such a situation, for each type of monomer, there will be subgroups of the molecular symmetry group that contain permutation operations which permute identical monomers. The group G_l which is the group that contains the permutations of identical monomers will be the direct product of these subgroups.

After a basis for a single monomer of one type of monomers is generated, the procedure of section III B can be used to generate bases for other monomers which are identical with

that monomer. The same thing can be done for each type of monomers, so that a basis for each monomer in the cluster is generated.

Once a basis for each monomer is generated, the procedures of sections IIIC and IIID can be used to combine the bases and to solve the problem. These steps has nothing to do with whether the monomers are identical or not.

B. Use of The Method with Pseudospectral Methods

Pseudospectral methods are used frequently in quantum mechanical calculations. In this type of methods, two different bases, which are usually isomorphic to each other, are used for the same degrees of freedom. Then, the different parts of the Hamiltonian are evaluated in the basis whichever is convenient for that part of the Hamiltonian.

If pseudospectral methods are used for evaluating the matrix elements of the Hamiltonian operator, then it becomes necessary to make transformations from one basis to another. This is achieved by using transformation matrices. For the monomer a , if $\phi_i^{(a)}$ with $i = 1, 2, \dots, N$ are basis functions in one of the bases and $\theta_i^{(a)}$ with $i = 1, 2, \dots, N$ are the basis functions in the second basis, then the relation between the basis functions of the two different bases will be

$$\phi_i^{(a)} = \sum_{j=1}^{j=N} T_{ij} \theta_j^{(a)} \quad (28)$$

where T_{ij} are the matrix elements of the transformation matrix T .

In section IIIB, it was seen that the proper way of generating bases for other monomers is to use the generator of the group which contains the operations that permute identical monomers. If the permutation operation P_{ab} is applied to the both sides of the equation above, by using equation (8) and the fact that matrix elements are just constants, the equation becomes

$$\phi_i^{(b)} = \sum_{j=1}^{j=N} T_{ij} P_{ab} \theta_j^{(a)} \quad (29)$$

Since the basis functions $\phi_i^{(b)}$ and $\phi_i^{(a)}$ are related to each other by equation (8) consistency requires that the same thing should be true for the basis functions $\theta_i^{(b)}$ and $\theta_i^{(a)}$, that is

$$\theta_i^{(b)} = P_{ab} \theta_i^{(a)}. \quad (30)$$

Thus, equation (29) becomes

$$\phi_i^{(b)} = \sum_{j=1}^{j=N} T_{ij} \theta_j^{(b)}. \quad (31)$$

Equations (28) and (31) show that if the basis functions of the monomers are related to each other with equation (8); then, the matrix elements of the transformation matrix for the bases of the monomer b will be the same with the matrix elements of the transformation matrix for the bases of the monomer a , so that both of the transformations can be done with the same transformation matrix. Consequently, while doing computations, it is not necessary to store separate transformation matrices for each monomer. The same transformation matrix can be used for all of the monomers of the same type. Since the transformation matrices usually occupy large memories especially if multidimensional coupled bases are used, this fact is very useful for reducing the memory cost of computations.

V. QUALITATIVE MODELS

In the following two subsections, two qualitative models will be given for the possible applications of the MBR method. The main discussion will be about the symmetries of wave functions. An implementation of the qualitative model given for water dimer will be made in a following paper for calculating its vibration-rotation-tunneling spectra.

A. Water Dimer

A group theoretical treatment of water dimer is done by Dyke and co-workers for explaining the microwave data [9]. The molecular symmetry group of this dimer is the group G_{16} which is isomorphic to the D_{4h} point group. If the oxygen atoms in the molecule are labeled as a and b ; the hydrogen atoms bonded to the oxygen a are labeled as 1 and 2; and the hydrogen atoms bonded to the oxygen b are labeled as 3 and 4; then, this group can be written as [11]

$$G_{16} = \left(\left(G_2^{(a)} \otimes G_2^{(b)} \right) \oplus G_2^{(ab)} \right) \otimes \varepsilon, \quad (32)$$

where the monomer permutation groups are

$$G_2^{(a)} = \{E, (12)\}, \quad (33)$$

$$G_2^{(b)} = \{E, (34)\}, \quad (34)$$

TABLE I: Character table of the permutation group G_2 .

G_2	E	(12)
A	1	1
B	1	-1

TABLE II: Character table of the inversion group ε .

ε	E	E^*
G	1	1
U	1	-1

the group containing the operations that permute the identical monomers is

$$G_2^{(ab)} = \{E, (ab)(13)(24)\}, \quad (35)$$

and the inversion group is

$$\varepsilon = \{E, E^*\}. \quad (36)$$

Character table of the group $G_2^{(a)}$ is given in table I. Character table of the group $G_2^{(b)}$ can be obtained from the character table of the group $G_2^{(a)}$ by replacing the operation (12) with the operation (34), since the two groups are isomorphic to each other. Similarly, the character table of the group $G_2^{(ab)}$ can be obtained from the character table of the group $G_2^{(a)}$ by replacing the operation (12) with the operation $(ab)(13)(24)$. Character table of the group ε is given in table II.

The monomer calculations should be done by symmetry adapting the basis functions to the irreducible representations of the group which is obtained as a direct product of the pure permutation group of the monomer and the inversion subgroup of the *cluster*. In the case of water dimer, if the monomer is chosen as the monomer a , this means that the monomer calculations should be done by symmetry adapting the basis functions to the irreducible representations of the group

$$C_{2v}(M) = G_2^{(a)} \otimes \varepsilon = \{E, (12), E^*, (12)^*\}. \quad (37)$$

Character table of the group $C_{2v}(M)$ is given in table III.

TABLE III: Character table of the $C_{2v}(M)$ permutation inversion group. This group is the direct product of the groups G_2 whose character table is given in table I and the group ε whose character table is given in table II. In the table, $\Gamma = x \otimes y$ means that the irreducible representation Γ of the group $C_{2v}(M)$ is obtained as direct product of the irreducible representation x of the group G_2 and the irreducible representation y of the group ε .

$C_{2v}(M) = G_2 \otimes \varepsilon$	E	(12)	E^*	$(12)^*$
$A_1 = A \otimes G$	1	1	1	1
$A_2 = A \otimes U$	1	1	-1	-1
$B_1 = B \otimes U$	1	-1	-1	1
$B_2 = B \otimes G$	1	-1	1	-1

After the monomer calculations are done with the basis which is symmetry adapted to the irreducible representations of the group $C_{2v}(M)$, the basis of the monomer b can be generated by using the generator of the group $G_2^{(ab)}$ which is $(ab)(13)(24)$. Then, the question becomes how to combine these bases for the solution of the full problem. Character table of the group G_{16} , which is the molecular symmetry group of water dimer, is given in table V. The correlations between the irreducible representations of the group G_{16} and the irreducible representations of its subgroups are given in table VI.

The monomer bases will already be symmetry adapted to the irreducible representations of the groups $G_2^{(a)}$ and $G_2^{(b)}$. Therefore, the product basis of monomer bases will be symmetry adapted in the group $G_4 = G_2^{(a)} \otimes G_2^{(b)}$, whose character table is given in table IV.

Considering the A_1^+ representation of the group G_{16} , the correlation table given in table VI says that this level correlates to Γ_1 irreducible representation of the group G_4 , A irreducible representation of the group $G_2^{(ab)}$ and G irreducible representation of the group ε . Therefore, if there is a basis for the monomers such that its basis functions are already symmetry adapted to the Γ_1 representation of the group G_4 , then these basis functions can be symmetry adapted to the irreducible representations of the group G_{16} by applying the projection operators of the A representation of the group $G_2^{(ab)}$ and the G representation of the group ε .

The Γ_1 irreducible representation of the group G_4 is the direct product of the A repre-

TABLE IV: Character table of the group G_4 . In the table, $\Gamma = x \otimes y$ means that the irreducible representation Γ of the group G_4 is obtained as a direct product of the irreducible representation x of the group $G_2^{(a)}$ and the irreducible representation y of the group $G_2^{(b)}$.

$G_4 = G_2^{(a)} \otimes G_2^{(b)}$	E	(12)	(34)	$(12)(34)$
$\Gamma_1 = A \otimes A$	1	1	1	1
$\Gamma_2 = A \otimes B$	1	1	-1	-1
$\Gamma_3 = B \otimes A$	1	-1	1	-1
$\Gamma_4 = B \otimes B$	1	-1	-1	1

TABLE V: Character table of the G_{16} PI group which is the molecular symmetry group of water dimer. This group is isomorphic to the D_{4h} point group. This character table is taken from a paper by Dyke [9].

	(12)	$(ab)(13)(24)$	$(ab)(1324)$	$(12)^*$	$(ab)(13)(24)^*$	$(ab)(1324)^*$				
G_{16}	E	(34)	$(ab)(14)(23)$	$(ab)(1423)$	$(12)(34)$	E^*	$(34)^*$	$(ab)(14)(23)^*$	$(ab)(1423)^*$	$(12)(34)^*$
A_1^+	1	1	1	1	1	1	1	1	1	1
A_2^+	1	-1	-1	1	1	1	-1	-1	1	1
B_1^+	1	1	-1	-1	1	1	1	-1	-1	1
B_2^+	1	-1	1	-1	1	1	-1	1	-1	1
E^+	2	0	0	0	-2	2	0	0	0	-2
A_1^-	1	1	1	1	1	-1	-1	-1	-1	-1
A_2^-	1	-1	-1	1	1	-1	1	1	-1	-1
B_1^-	1	1	-1	-1	1	-1	-1	1	1	-1
B_2^-	1	-1	1	-1	1	-1	1	-1	1	-1
E^-	2	0	0	0	-2	-2	0	0	0	2

sentation of the group $G_2^{(a)}$ and the A representation of the group $G_2^{(b)}$. Therefore, the direct product of the monomer bases which are symmetry adapted to the A representations in their own permutation groups will be symmetry adapted to the Γ_1 irreducible representation of

TABLE VI: Correlations between the irreducible representations of the group G_{16} and its subgroups.

G_{16}	G_4	$G_2^{(ab)}$	ε
A_1^+	Γ_1	A	G
A_2^+	Γ_4	B	G
B_1^+	Γ_1	B	G
B_2^+	Γ_4	A	G
E^+	$\Gamma_2 \oplus \Gamma_3$	$A \oplus B$	G
A_1^-	Γ_1	A	U
A_2^-	Γ_4	B	U
B_1^-	Γ_1	B	U
B_2^-	Γ_4	A	U
E^-	$\Gamma_2 \oplus \Gamma_3$	$A \oplus B$	U

the group G_4 .

The monomer calculations are done with the group $C_{2v}(M)$. In this group both of the irreducible representations A_1 and A_2 contains the A representation of the group $G_2^{(a)}$, therefore both of the bases which are symmetry adapted to the irreducible representations A_1 and A_2 of the group $C_{2v}(M)$ can be used for the monomer a , so that the basis of the monomer a should be $A_1 \oplus A_2$, where the labels of the irreducible representations are used to imply basis functions belonging to that symmetry. The same thing will be true also for the monomer b . Thus, there will be four different product bases which will be symmetry adapted to the irreducible representation Γ_1 of the group G_4 which are: $A_1 \otimes A_1$, $A_1 \otimes A_2$, $A_2 \otimes A_1$, $A_2 \otimes A_2$.

The character of the operation E^* is 1 in the irreducible representation A_1 and -1 in the irreducible representation A_2 . Therefore, the basis functions included in the product bases $A_1 \otimes A_1$ and $A_2 \otimes A_2$ will not change sign upon the operation of the inversion operation E^* , so that they will have even parity. On the other hand the basis functions included in the product bases $A_1 \otimes A_2$ and $A_2 \otimes A_1$ will change sign upon the operation of the inversion operation E^* , so that they will have odd parity. In order to fully symmetry adapt the these

TABLE VII: This table shows which monomer bases should be combined for obtaining bases for water dimer calculations with the group G_{16} . In the table, labels of the irreducible representations are used to imply basis functions belonging to that symmetry. For an explanation of how to obtain mutually orthogonal basis for the doubly degenerate levels (i.e. E_x^+ , E_y^+) see reference [11].

G_{16}	Bases	G_{16}	Bases
A_1^+	$(A_1 \otimes A_1) \oplus (A_2 \otimes A_2)$	A_1^-	$(A_1 \otimes A_2) \oplus (A_2 \otimes A_1)$
A_2^+	$(B_1 \otimes B_1) \oplus (B_2 \otimes B_2)$	A_2^-	$(B_1 \otimes B_2) \oplus (B_2 \otimes B_1)$
B_1^+	$(A_1 \otimes A_1) \oplus (A_2 \otimes A_2)$	B_1^-	$(A_1 \otimes A_2) \oplus (A_2 \otimes A_1)$
B_2^+	$(B_1 \otimes B_1) \oplus (B_2 \otimes B_2)$	B_2^-	$(B_1 \otimes B_2) \oplus (B_2 \otimes B_1)$
E_x^+	$(A_1 \otimes B_2) \oplus (A_2 \otimes B_1)$	E_x^-	$(A_1 \otimes B_1) \oplus (A_2 \otimes B_2)$
E_y^+	$(B_2 \otimes A_1) \oplus (B_1 \otimes A_2)$	E_y^-	$(B_1 \otimes A_1) \oplus (B_2 \otimes A_2)$

basis functions to the A_1^+ irreducible representation of the group G_{16} , it is necessary to apply the projection operator of the G irreducible representation of the group ε , which is $P_\varepsilon^G = (E + E^*)/2$. Since the basis functions in the product bases $A_1 \otimes A_1$ and $A_2 \otimes A_2$ does not change sign upon the operation of the inversion operator, these basis functions will be invariant under the effect of the projection operator P_ε^G . On the other hand, since the basis functions in the product bases $A_1 \otimes A_2$ and $A_2 \otimes A_1$ change sign upon the operation of the inversion operation, they will be annihilated when the projection operator P_ε^G is applied. Therefore, among the four product bases which are symmetry adapted to the Γ_1 irreducible representation of the group Γ_1 , only the bases $A_1 \otimes A_1$ and $A_2 \otimes A_2$ can be used for the calculations of the A_1^+ representation of the group G_{16} .

Thus, the way to generate a basis for the calculations of the A_1^+ representations of the group G_{16} is to take the product bases $A_1 \otimes A_1$ and $A_2 \otimes A_2$ and symmetry adapt them to the irreducible representation A_1^+ of the group G_{16} by applying the projection operator $P_{G_2^{(ab)}}^A$ of the group $G_2^{(ab)}$. Application of the projection operator P_ε^G will already leave the basis functions invariant.

Similarly, the way to combine the monomer bases for the other irreducible representations of the group G_{16} can be found. The results are summarized in table VII.

TABLE VIII: Character table of the group G_{24} . This table is taken from a paper by van der Avoird *et. al.* [15]. In the table, representations given as A_{2g} , A_{3g} , A_{2u} and A_{3u} in that article are combined to the doubly degenerate representations $E_g = A_{2g} \oplus A_{3g}$ and $E_u = A_{2u} \oplus A_{3u}$. In contrast to the reference [15], operations in the classes are shown explicitly.

		$(acb)(164253)$	$(abc)(135264)$	$(acb)(153)(264)$	$(abc)(135)(246)$			
		$(acb)(153264)$	$(abc)(146235)$	$(acb)(164)(253)$	$(abc)(146)(235)$	(12)	$(12)(34)$	
		$(acb)(154263)$	$(abc)(145236)$	$(acb)(154)(263)$	$(abc)(145)(236)$	(34)	$(12)(56)$	
	E	$(acb)(163254)$	$(abc)(136245)$	$(acb)(163)(254)$	$(abc)(136)(245)$	(56)	$(34)(56)$	$(12)(34)(56)$
A_{1g}	1	1	1	1	1	1	1	1
E_g	2	-1	-1	-1	-1	2	2	2
T_g	3	0	0	0	0	-1	-1	3
A_{1u}	1	-1	-1	1	1	-1	1	-1
E_u	2	1	1	-1	-1	-2	2	-2
T_u	3	0	0	0	0	1	-1	-3

B. Water Trimer

A group theoretical treatment of water trimer is done by van der Avoird *et. al.* [15]. The molecular symmetry group of water trimer is the group G_{48} . This group is the direct product of the inversion subgroup and the pure permutation subgroup G_{24} , such that $G_{48} = G_{24} \otimes \varepsilon$. Character table of the group G_{24} is given in table VIII. In the table a, b, c are the labels for the oxygen atoms. The hydrogen atoms bonded to oxygen a are labeled as 1 and 2, the hydrogen atoms bonded to oxygen b are labeled as 3 and 4, and the hydrogen atoms bonded to oxygen c are labeled as 5 and 6.

If follows from equation (3), the molecular symmetry group of water trimer can be written in terms of its subgroups as [11]

$$G_{48} = \left(\left(G_2^{(a)} \otimes G_2^{(b)} \otimes G_2^{(c)} \right) \otimes G_3 \right) \otimes \varepsilon, \quad (38)$$

where the pure permutation groups of the monomers are

$$G_2^{(a)} = \{E, (12)\}, \quad (39)$$

$$G_2^{(b)} = \{E, (34)\}, \quad (40)$$

$$G_2^{(c)} = \{E, (56)\}, \quad (41)$$

and the group containing the operations permuting the monomers is

$$G_3 = \{E, (abc)(135)(246), (acb)(153)(264)\}. \quad (42)$$

Character table of the group G_3 is given in table IX.

TABLE IX: Character table of the group G_3 . In the table, $w = \exp(2i\pi/3)$.

G_3	E	$(abc)(135)(246)$	$(acb)(153)(264)$
A	1	1	1
E_x	1	w	w^*
E_y	1	w^*	w

As long as the symmetry adaptation of the monomer calculations are concerned, there is no difference between water dimer and water trimer. The monomer calculations should be done by symmetry adapting the basis functions to the irreducible representations of the group $C_{2v}(M) = G_2^{(a)} \otimes \varepsilon$. After the monomer calculations are done, bases of monomer b can be generated from the bases of monomer a by using the permutation operation $(abc)(135)(246)$. The bases of the monomer c can be generated either from the bases of the monomer a by using the permutation operation $(acb)(153)(264)$ or from the bases of the monomer b by using the permutation operation $(abc)(135)(246)$.

Since the monomer bases functions are already symmetry adapted in their own permutation groups, the product basis of the monomer bases will be symmetry adapted in the group $G_8 = G_2^{(a)} \otimes G_2^{(b)} \otimes G_2^{(c)}$. Character table of the group G_8 is given in table X. The correlations between the irreducible representations of the group G_{48} and its subgroups G_8 , G_3 and ε are given in table XI.

In order to illustrate how the monomer bases can be combined for the solution of the full problem consider the E_g^+ representation. This representation correlates to the Γ_1 representation of the group G_8 . Since the irreducible representation Γ_1 is obtained as a direct product

TABLE X: Character table of the group G_8 . Correlations with the irreducible representations of the subgroups are indicated such that in the table $\Gamma = x \otimes y \otimes z$ means that the irreducible representation Γ of the group G_8 is obtained as a direct product of the irreducible representations x , y and z of the groups $G_2^{(a)}$, $G_2^{(b)}$ and $G_2^{(c)}$, respectively.

$G_8 = G_2^{(a)} \otimes G_2^{(b)} \otimes G_2^{(c)}$	E	(12)	(34)	(56)	(12)(34)	(12)(56)	(34)(56)	(12)(34)(56)
$\Gamma_1 = A \otimes A \otimes A$	1	1	1	1	1	1	1	1
$\Gamma_2 = A \otimes A \otimes B$	1	1	1	-1	1	-1	-1	-1
$\Gamma_3 = A \otimes B \otimes A$	1	1	-1	1	-1	1	-1	-1
$\Gamma_4 = B \otimes A \otimes A$	1	-1	1	1	-1	-1	1	-1
$\Gamma_5 = A \otimes B \otimes B$	1	1	-1	-1	-1	-1	1	1
$\Gamma_6 = B \otimes A \otimes B$	1	-1	1	-1	-1	1	-1	1
$\Gamma_7 = B \otimes B \otimes A$	1	-1	-1	1	1	-1	-1	1
$\Gamma_8 = B \otimes B \otimes B$	1	-1	-1	-1	1	1	1	-1

of the A representations of the pure permutation groups of the monomers (see table XI), the product basis of the monomer bases which are symmetry adapted to the A representation should be used for forming the monomer bases for the solution of the full problem. Since the monomer calculations are done with the group $C_{2v}(M)$, both of the A_1 and A_2 representations are symmetry adapted to the A representation of the pure permutation group of the monomers. Therefore, the monomer bases that should be used in the calculations is the sum of A_1 and A_2 bases which is $A_1 \oplus A_2$, and the product basis of the monomer bases is going to be

$$(A_1 \oplus A_2) \otimes (A_1 \oplus A_2) \otimes (A_1 \oplus A_2).$$

When the multiplications are done, there will be eight terms. Half of them will have even parity and half of them will have odd parity. The functions having odd parity will be annihilated upon the operation of the projection operator P_ϵ^G of the inversion group. On the other hand the functions having even parity will be invariant under the effect of the projection operator P_ϵ^G . Thus, only the terms which have the right parity will lead to basis for the full problem. These bases are $(A_1 \otimes A_1 \otimes A_1) \oplus (A_1 \otimes A_2 \otimes A_2) \oplus (A_2 \otimes A_1 \otimes A_2) \oplus (A_2 \otimes A_2 \otimes A_1)$. After these bases are combined with a basis related with inter-monomer

TABLE XI: Correlations between the irreducible representations of the group G_{48} and its subgroups.

G_{48}	G_8	G_3	ε
A_{1g}^+	Γ_1	A	G
E_g^+	$2 * \Gamma_1$	$E_x \oplus E_y$	G
T_g^+	$\Gamma_5 \oplus \Gamma_6 \oplus \Gamma_7$	$A \oplus E_x \oplus E_y$	G
A_{1u}^+	Γ_8	A	G
E_u^+	$2 * \Gamma_8$	$E_x \oplus E_y$	G
T_u^+	$\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$	$A \oplus E_x \oplus E_y$	G
A_{1g}^-	Γ_1	A	U
E_g^-	$2 * \Gamma_1$	$E_x \oplus E_y$	U
T_g^-	$\Gamma_5 \oplus \Gamma_6 \oplus \Gamma_7$	$A \oplus E_x \oplus E_y$	U
A_{1u}^-	Γ_8	A	U
E_u^-	$2 * \Gamma_8$	$E_x \oplus E_y$	U
T_u^-	$\Gamma_2 \oplus \Gamma_3 \oplus \Gamma_4$	$A \oplus E_x \oplus E_y$	U

coordinates, they can be symmetry adapted to the E_g^+ irreducible representation of the group G_{48} by application of the projection operator $P_{G_3}^{E_x} + P_{G_3}^{E_y}$.

Similarly, the monomer bases which should be used to form a product basis for each irreducible representation of the group G_{48} can be found. The results are given in table XII.

VI. CONCLUSIONS

By using the sequential symmetry adaptation procedure, and the physically meaningful partitioning of the molecular symmetry group of molecular clusters, a new method for calculating the VRT spectra of molecular clusters named Monomer Basis Representation (MBR) method was developed in section III. In the MBR method, calculations starts with a single monomer with the purpose of obtaining an optimized basis for that monomer as a linear combination of some primitive basis functions. Then, an optimized basis for each identical monomer is generated from the optimized basis of this monomer. By using the optimized

TABLE XII: This table shows which monomer bases should be combined for obtaining bases for the calculations of the water trimer with the group G_{48} . In the table labels of the irreducible representations are used to imply the monomer basis functions belonging to that symmetry. For an explanation of how to obtain mutually orthogonal bases for the triply degenerate levels (i.e. T_{gx}^+ , T_{gy}^+ , T_{gz}^+), see reference [11].

G_{48} Bases	
A_{1g}^+	$(A_1 \otimes A_1 \otimes A_1) \oplus (A_1 \otimes A_2 \otimes A_2) \oplus (A_2 \otimes A_1 \otimes A_2) \oplus (A_2 \otimes A_2 \otimes A_1)$
E_g^+	$(A_1 \otimes A_1 \otimes A_1) \oplus (A_1 \otimes A_2 \otimes A_2) \oplus (A_2 \otimes A_1 \otimes A_2) \oplus (A_2 \otimes A_2 \otimes A_1)$
T_{gx}^+	$(A_1 \otimes B_2 \otimes B_2) \oplus (A_1 \otimes B_1 \otimes B_1) \oplus (A_2 \otimes B_2 \otimes B_1) \oplus (A_2 \otimes B_1 \otimes B_2)$
T_{gy}^+	$(B_2 \otimes B_2 \otimes A_1) \oplus (B_1 \otimes B_1 \otimes A_1) \oplus (B_2 \otimes B_1 \otimes A_2) \oplus (B_1 \otimes B_2 \otimes A_2)$
T_{gz}^+	$(B_2 \otimes A_1 \otimes B_2) \oplus (B_1 \otimes A_1 \otimes B_1) \oplus (B_1 \otimes A_2 \otimes B_2) \oplus (B_2 \otimes A_2 \otimes B_1)$
A_{1u}^+	$(B_2 \otimes B_2 \otimes B_2) \oplus (B_2 \otimes B_1 \otimes B_1) \oplus (B_1 \otimes B_2 \otimes B_1) \oplus (B_1 \otimes B_1 \otimes B_2)$
E_u^+	$(B_2 \otimes B_2 \otimes B_2) \oplus (B_2 \otimes B_1 \otimes B_1) \oplus (B_1 \otimes B_2 \otimes B_1) \oplus (B_1 \otimes B_1 \otimes B_2)$
T_{ux}^+	$(A_1 \otimes A_1 \otimes B_2) \oplus (A_1 \otimes A_2 \otimes B_1) \oplus (A_2 \otimes A_1 \otimes B_2) \oplus (A_2 \otimes A_2 \otimes B_2)$
T_{uy}^+	$(A_1 \otimes B_2 \otimes A_1) \oplus (A_2 \otimes B_1 \otimes A_1) \oplus (A_1 \otimes B_2 \otimes A_2) \oplus (A_2 \otimes B_2 \otimes A_2)$
T_{uz}^+	$(B_2 \otimes A_1 \otimes A_1) \oplus (B_1 \otimes A_1 \otimes A_2) \oplus (B_2 \otimes A_2 \otimes A_1) \oplus (B_2 \otimes A_2 \otimes A_2)$
A_{1g}^-	$(A_2 \otimes A_2 \otimes A_2) \oplus (A_1 \otimes A_1 \otimes A_2) \oplus (A_1 \otimes A_2 \otimes A_1) \oplus (A_2 \otimes A_1 \otimes A_1)$
E_g^-	$(A_2 \otimes A_2 \otimes A_2) \oplus (A_1 \otimes A_1 \otimes A_2) \oplus (A_1 \otimes A_2 \otimes A_1) \oplus (A_2 \otimes A_1 \otimes A_1)$
T_{gx}^-	$(A_2 \otimes B_1 \otimes B_1) \oplus (A_1 \otimes B_2 \otimes B_1) \oplus (A_1 \otimes B_1 \otimes B_2) \oplus (A_2 \otimes B_2 \otimes B_2)$
T_{gy}^-	$(B_1 \otimes B_1 \otimes A_2) \oplus (B_2 \otimes B_1 \otimes A_1) \oplus (B_1 \otimes B_2 \otimes A_1) \oplus (B_2 \otimes B_2 \otimes A_2)$
T_{gz}^-	$(B_1 \otimes A_2 \otimes B_1) \oplus (B_1 \otimes A_1 \otimes B_2) \oplus (B_2 \otimes A_1 \otimes B_1) \oplus (B_2 \otimes A_2 \otimes B_2)$
A_{1u}^-	$(B_1 \otimes B_1 \otimes B_1) \oplus (B_2 \otimes B_2 \otimes B_1) \oplus (B_2 \otimes B_1 \otimes B_2) \oplus (B_1 \otimes B_2 \otimes B_2)$
E_u^-	$(B_1 \otimes B_1 \otimes B_1) \oplus (B_2 \otimes B_2 \otimes B_1) \oplus (B_2 \otimes B_1 \otimes B_2) \oplus (B_1 \otimes B_2 \otimes B_2)$
T_{ux}^-	$(A_2 \otimes A_2 \otimes B_1) \oplus (A_1 \otimes A_1 \otimes B_1) \oplus (A_1 \otimes A_2 \otimes B_2) \oplus (A_2 \otimes A_1 \otimes B_2)$
T_{uy}^-	$(A_2 \otimes B_1 \otimes A_2) \oplus (A_1 \otimes B_1 \otimes A_1) \oplus (A_2 \otimes B_2 \otimes A_1) \oplus (A_1 \otimes B_2 \otimes A_2)$
T_{uz}^-	$(B_1 \otimes A_2 \otimes A_2) \oplus (B_1 \otimes A_1 \otimes A_1) \oplus (B_2 \otimes A_1 \otimes A_2) \oplus (B_2 \otimes A_2 \otimes A_1)$

bases of the monomers, a basis is generated for the solution of the full problem, and the VRT spectra of the cluster is obtained by using this basis. Since an optimized basis is used for each monomer which has a much smaller size than the primitive basis from which the

optimized bases are generated, the MBR method leads to an exponential decrease in the size of the basis that is required for the convergence of the results.

The generation of an optimized basis for each monomer as a linear combination of some primitive basis functions led to two problems related with the symmetry adaptation. When a basis for the solution of the full problem is obtained as a direct product of the optimized monomer bases. These basis functions should still be symmetry adapted to the inversion group and also to the group which contains the permutations of the monomers. In order to symmetry adapt basis functions to these groups, it is necessary to apply the symmetry operations contained in these groups to the basis functions. When these operations are applied to the basis functions, the resulting functions should already be in the basis in order to have an orthogonal basis. However, when the monomer basis functions are linear combinations of some primitive basis functions, the functions obtained as a result of the operations of the permutation inversion operations will not be necessarily in the same basis.

It has been suggested that the invariance of the basis functions under the effect of the inversion operation can be achieved by symmetry adapting primitive monomer basis functions to the inversion subgroup while generating the optimized basis for the monomers. If the monomer basis functions are already symmetry adapted to the inversion subgroup, then they will be eigenstates of the inversion operator with the eigenvalues ± 1 . Consequently, the basis functions which are obtained as a direct product of the monomer basis functions will be the eigenstates of the inversion operator with the eigenvalues ± 1 . Thus, the basis which is obtained as a direct product of the optimized monomer bases becomes invariant under the effect of the inversion operation.

It has also been shown that the product basis of the optimized monomer bases can be made invariant under the effect of the operations permuting identical monomers by finding an optimized basis for a single monomer and then generating bases for other monomers from the basis of that monomer. If an optimized basis for each monomer is generated separately independent of other monomer bases, then there is no way to guarantee the invariance of the basis. On the other hand, if all of the monomer bases are generated from a single monomer basis, then it is possible to correlate the bases to each other so that the product basis of optimized monomer bases becomes invariant. It has been shown that a basis for all of the monomers can be generated from the basis on a single monomer by repeated application of the generator of the group G_l which is the group containing the operations that permute

identical monomers. This way of generating bases for all of the monomers made it necessary to assume that the order of the group G_l is equal to the number of the monomers: $G_l = n_m$.

While developing the method, the primitive bases of the monomers were never referenced. Thus, the nature of the primitive monomer bases does not matter. They can be product bases of one dimensional bases, or they can be multidimensional coupled bases. The symmetry adaptation procedure given here will work regardless of the nature of the primitive bases used in the monomer calculations.

Another point which is not discussed in detail in the development of the method was what should be the model potential surface while generating a monomer basis. This is just because it is impossible to suggest a perfect model potential surface regardless of the particular problem being studied. The model potential surface should be chosen according to the problem at hand. Nevertheless it should be noted that the more the model potential resembles to the actual problem, the more efficient the monomer bases will be.

Decomposition Of Projection Operators

In order to find a relation between the projection operators of a product group and the projection operators of its subgroups, it is necessary to find a relation between the characters of the elements of the product group and the characters of the elements of the subgroups. Such a relation can be derived from the following character equation which holds in any irreducible representation of any group [16]:

$$N_i \chi(C_i) N_j \chi(C_j) = d \sum_k c_{ijk} N_k \chi(C_k). \quad (43)$$

In the equation above, C_i , C_j and C_k are classes of the group; N_i , N_j and N_k are the number of elements in these classes; and the coefficients c_{ijk} are defined by the class multiplication equation $C_i C_j = \sum_k c_{ijk} C_k$; and d is the dimension of the irreducible representation.

Consider a group G that can be written as a semi-direct product of two of its subgroups H and K such that $G = H \otimes K$. If h is an element of group H that is in class C_i of the group G and k is an element of the group K that is in class C_j of the group G , and $g = hk$ is an element of the group G that is in class C_m ; then provided that the class multiplication constants satisfy the equation

$$c_{ijk} = r \delta_{km}, \quad (44)$$

where r is an integer; equation (43) reduces to

$$\chi(h)\chi(k) = d\chi(g), \tag{45}$$

and equation (5) follows. Consequently, equation (44) is the sufficient condition that the sequential symmetry adaptation will work for any irreducible representation of the product group. This equation seems to be satisfied in many cases for the physically meaningful partitioning of the molecular molecular symmetry group of molecular clusters given in equation (3). The examples include molecular symmetry groups of the clusters $(H_2O)_2$, $(CO_2)_2$, $(H_2O)_3$, $(H_2O)_2D_2O$. However, although it has been argued before [11] that the equation (44) holds for any irreducible representation of any semi-direct product group, this is not the case. For example, if pairwise permutations of monomers would be a feasible symmetry operation for water trimer so that the molecular symmetry group would be G_{96} instead of G_{48} , then equation (44) would not hold for the semi-direct product multiplication defined by equation (3).

It should also be noted that equation (45) holds for any one dimensional representation. This follows from the fact that one dimensional representations are representations by nonzero complex numbers and a representation should satisfy equation (45) by definition of representation since the characters of the elements are just the complex numbers representing them. Consequently, even if the condition given in equation (44) does not hold, sequential symmetry adaptation can still be used for one dimensional representations.

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